

# Obtaining a Bioadsorbent from Orange Peel suitable for Batch and Continuous Treatment

García Raurich, Josep<sup>1</sup>; Martínez Roldán, Tania<sup>2</sup>; Monagas Asensio, Pedro<sup>3</sup>

CRESCA (Centre de Recerca en Seguretat i Control Alimentari of the UPC). ESEIAAT Colom 1, 08222-Terrassa (Barcelona)

**Abstract**— One form of chemical contamination involves the contribution of heavy metals to the ecosystem mainly from industrial spills and mining operations. The most toxic heavy metals are cadmium, copper, chromium, mercury, nickel, lead and zinc. The importance of this type of toxic lies in the tendency to be accumulated and concentrated by the different species, being more dangerous as it ascends the evolutionary chain towards man.

Chemical precipitation is the most widely used technique for metal recovery. This process is conditioned by the pH, metal concentration and anions present in the water to be treated.

Bioadsorption is considered a viable alternative to the physico-chemical methods currently used for the recovery or removal of heavy metals dissolved in liquid effluents. Its main attractiveness, from an industrial point of view, is its low cost due to the great abundance, easy obtaining and low price of the bioadsorbent material. Bioadsorption is very effective in the treatment of metal concentrations below 100 mg/L, where the application of physical-chemical methods is not technically and economically feasible.

One of these materials of interest is orange peels because, due to their abundance as a waste product of the food industries, they have problems for their disposal and currently have little economic value. However, this residue has a low adsorption capacity, so both physical and chemical modifications are required to increase its adsorption properties.

The objective of this work has been to optimize the treatment of orange peel intended to obtain a bioadsorbent that allows the removal of heavy metals both in a discontinuous process (Batch) and in an ongoing process. The verification of the characteristics of the bioadsorbent obtained has been carried out with a series of synthetic solutions of Cu (II).

The particle size and consistency of the final bioadsorbent has been optimized. In addition, to achieve a homogeneous elution in the continuous process, additional heat treatment has been necessary to prevent the development of microorganisms in a period of time less than one week.

**Keywords**— bioadsorption, orange peel, heavy metal removal.

## I. INTRODUCTION

The described wastewater treatment techniques are divided into three sections: a) Separation or clarification techniques, which are mainly used in combination with other operations, or as a first step (to protect other facilities treatment against damage, obstruction or solids fouling) or a final clarification step (to remove solids or oil formed during a previous treatment operation). b) Physicochemical treatment techniques for non-biodegradable wastewater, mainly used for inorganic or non-biodegradable organic contaminants. c) Biological treatment techniques for biodegradable wastewater (Ministry of Environment, rural and marine environment of Spain 2009).

Traditionally, the elimination (but non-recovery) of heavy metals present in wastewater from industrial processes has been carried out in a majority way through precipitation processes of these metals as hydroxides in the middle basic. This technique has two drawbacks: on the one hand, the high solubility of some of the formed species, which entails a low elimination of the metal of interest of the dissolution to be treated and, therefore, requires a post-treatment that adjusts the concentration of heavy metal in the effluent to the environmental regulations of discharge, and on the other, the management of the sludge generated, which contain high concentrations of metal ions. The usual precipitation agents are: lime (calcium hydroxide), caustic soda, sulphides and sodium and calcium carbonates (Metcalf & Eddy, 2014). In most cases, calcium hydroxide is the most effective reagent because it results in the formation of very stable precipitates and has the ability to destabilize colloids.

Alternatively, among several methods, adsorption is one of the treatments most accepted for its versatility and simplicity. This technique, based on a physical process that is produced by weak long-range interactions (van der Waals forces), allows

particles, molecules, or ions to be trapped or retained on the surface of a material, is highly effective for the removal of heavy metals has removal of a wide variety of contaminants, with rapid kinetics (Liu & Lee, 2014).

In the removal processes it is sought to prevent molecules from transforming or degrading, by breaking or by exchange of functional groups, avoiding the generation of compounds more reactive and toxic than the original compound (Sivaraj, et al; 2001).

Because of its high organic matter adsorption capacity, activated carbon is the most widely used adsorbent material, so it is considered a conventional adsorbent (McDougall 1991), having prepared different types of activated carbons from walnut shells (Yalcin & Sevinc 2000), eucalyptus bark (Bello, et al. 2002), corn cobs (Abdel-Nasser, et al. 2001), and other residues. However, its high cost of production limits its application in wastewater treatment. Clays, biopolymers, zeolites, silica beads and plants or lignocellulosic wastes are some of the adsorbents, commonly used to remove ion dyes, heavy metals, radioactive materials among other organic pollutants and generated by different types of industries (Osei Boamah, et al; 2015).

Bioadsorption is the application of low-cost materials obtained from different biomasses from microbial flora, algae and agro-industrial waste to replace the use of conventional methods in the removal of contaminants (Hala, 2013). Bioadsorption has emerged as an ecological alternative to conventional technologies for the treatment of effluents containing concentrations of diluted metal (Suresh et al., 2015). It is usually applied in the removal of heavy metals by passive binding to non-living biomass from aqueous solutions (Feng et al., 2011).

Currently, the term bioadsorption, is used to describe the phenomenon of passive uptake of pollutants, based on the property that certain types of inactive or dead biomass possess to bind and accumulate different types of contaminants. This accumulation does not occur by metabolic mechanisms, which is what happens in bioaccumulation and that occurs with living cells (Adebayo et al., (2018).

The biomaterials used in these processes (rice, orange, lemon, etc.) act in short contact times and generate high quality effluents by different mechanisms (Sharma et al., 2007). In the presence of heavy metals, the most widely accepted mechanism is the ion exchange (Davis et al., 2003). Recently, new types of biomaterials have been introduced (Ouldoumna et al., 2013).

Another area of bioadsorption use as an alternative process (economic and with an acceptable environmental impact) is that of wastewater in the textile industry (Sivaraj, et al 2001). Traditionally, these wastewaters have been treated with physical and chemical processes that are expensive to remove the dyes present. These processes incur operating and maintenance costs that most small industries cannot absorb (Lu et al., 2010). Bioadsorption mechanisms in this field are being investigated and it has been found preliminarily to be by complexation, ion exchange, or by formation of hydrogen bonds (Zumriye 2005).

The bioadsorption process involves a solid phase (biomass) and a liquid phase (water) containing dissolved substance of interest that will be adsorbed (in this case,  $\text{Cu}^{2+}$  ions). In order for the bioadsorption process to be successful, there must be a strong affinity between the functional groups of biomass and the contaminant, since the latter must be attracted to the solid and bound by different mechanisms (Chojnacka 2010). In all cases, biosorption processes depend on the nature of the substance to be removed, the structure and characteristics of the bioadsorbent (specific area, diameter and volume of pores, surface loading, active sites, chemical composition) and experimental conditions (Gautam, et al.2014).

One of these materials of interest is orange peels because, due to their abundance as a waste product of the food industries, they have problems for their disposal and currently have little economic value. However, this residue has a low adsorption capacity, so both physical and chemical modifications are required to increase its adsorption properties (Feng, et al 2010), (Left, et al 2013). However, many by-products can be obtained such as essential oils, carotenoids, flavourings and other derivatives applicable in the food, pharmaceutical and cosmetic industries (Pacheco, et al. 2019).

## II. MATERIALS, METHODS AND RESULTS

The transformation of orange peel as a cation exchanger requires a physical-chemical treatment.

### 2.1 Treatment of orange peel

This process begins with the collection and cleaning of oranges. It is important to select well-conditioned orange peels, i.e. without fungi, worms or decaying parts. The edible part (endocarp) is then separated, so that the shell (flavelo and albedo) is

freed from the pulp residues and is cleaned with detergent. In this way, waxes are extracted that, superficially, are incorporated to improve the appearance of this fruit in the commercial circuit.

After being dried with forced air and brought to the stove at a temperature of 32°C to constant weight, it is crushed and sieved, selecting those of a size between 500 µm and 1000 µm (Figure 1).



**FIGURE 1: Orange peel fitness process**

Physical modifications involve adequate sizing of orange peel by cutting or crushing, complemented by heat treatments such as reflux, microwave or ultrasonic irradiation.

On the other hand, chemical modifications include treatment with different types of chemical agents, which are used to increase binding groups in the final bioadsorbent, eliminate inhibitory groups and increase their surface area (Patel, 2012).

Lignocellulosic materials are mostly composed of cellulose, hemicellulose, pectin and lignin. These long-chain polymers, branched or linear, are present in the cell walls of plants and are the main responsible for adsorption of both metal ions (Galant et al., 2014) and macromolecules (Xu et al., 2013) and is the main responsibility of adsorption of both metal ions (Galant et al., 2014) and macromolecules (Xu et al., 2013) and is the it is necessary to know the functional groups that they possess and their affinity for metal ions, because the efficiency of the process will depend on it (Ysambertt, et al., 2009).

The chemical treatment begins with a process of acidification of the shells by hydrochloric acid, aimed at the extraction of pectin. Although the sourcing of pectin from orange peels has been extensively studied (Fishman et al., 2003), (Msebahi et al., 2005), (Liu et al., 2006), (Yeoh et al., 2008), the extraction of pectins by conventional methods is carried out at nearby temperatures at 90 °C for at least one hour in acidic aqueous solutions (Fishman & Cooke, 2009), so that the pectins that are not sensitive to calcium are extracted. After a while, the resulting solution is removed from the non-soluble body by filtration. It is then mixed with alcohol and precipitates the pectin (Claus, 2002).

The extraction of soluble pectin in acidic medium is necessary for its ability to form colloids and has the property of absorbing a large amount of water. If it is not extracted, the final product would not have the sufficient degree of consistency to be used as a bioadsorbent. Along with pectin, acid hydrolysis involves solubilization and degradation of carbohydrates, especially xylan and hemicellulose, as glucomanane is relatively stable in acid medium (Van Buren, 1991).

From previous experiences (Sundararaman et al., 2016), (Arjona et al., 2018), the chemical attack of orange peel is performed by ultrasonic radiation (US), using a US Elmasonic model LC 30 H bath with a fixed frequency of 37,5kHz and regulation of time and temperature, for a period of 45 minutes.

The acidic treatment is repeated until a solid is free of sugars and soluble pectin, as well as the soluble hemicellulose fraction under these experimental conditions. A repetition is usually sufficient for the sugar reduction test (Fehling method) to be negative. It should be remembered that carbohydrates are components of cell walls and are part of the structural matrix (Carpita & McCann 2000).

Once the pectin is extracted, the acid-soluble hemicellulose and the reducing sugars, a treatment with distilled water is performed, to remove the excess hydrochloric acid initially used. The resulting body is then treated in a basic medium. In this way, saponification of non-soluble pectin in acid medium is achieved, as well as the solubilization of the soluble fraction of hemicellulose in alkaline medium (Grace et al., 1996). It is proven (Arjona et al., 2018), (García Raurich et al., 2019) that the saponification and cross linking process can be carried out in a single stage with the use of a  $\text{Ca(OH)}_2$  0.2 M solution.

The saponification and crosslinking process is also performed in the US Elmasonic bathroom model LC 30 H for a period of 45 minutes. After this treatment, excess  $\text{Ca(II)}$  is removed by washing with distilled water. The bioadsorbent obtained is dried and ground to a final particle size product between 500-1000 µm and kept in a hermetically sealed container. Table 1 shows the mean values (3 repetitions) of the organic matter removed in acidic treatments and alkaline treatment. The results were obtained by the action of  $\text{KMnO}_4$  in sulphuric medium (permanganometry) and expressed as  $\text{mg O}_2/\text{L}$ .

**TABLE 1**  
**ORGANIC MATTER EXTRACTED AT EACH ATTACK (mg O<sub>2</sub>/L)**

First acid attack	Second acid attack	Alkaline attack
103,75 ± 1,4	68,8 ± 2,1	34,4 ± 4

It can be seen as much more effective the first acid attack than the second and, moreover, that the extraction of organic matter in the alkaline attack is significantly lower.

## 2.2 Increase in Ca(II) in the final bioadsorbent

The Ca(II) present in orange peel samples was determined and compared with the Ca(II) content in the final bioadsorbent. The granulometry was set at 500-1000 m and samples underwent a calcination process at 570 °C inside a Hobersal JB 20 laboratory muffle furnace for 4 hours.

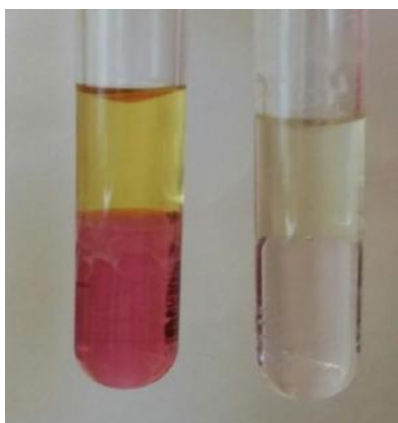
The determination of Ca(II) and Mg(II) was performed volumetrically, after solubilization of the corresponding ashes. As a titrant, 0.01M EDTA (ethylenediaminetetraacetic acid) and NET (Eriochrome T Black) were used as indicator. First, the total amount of Ca(II) and Mg (II) were determined. In another aliquot, Ca(II) was precipitated with oxalic acid 0.05M and then the complexometric titration was repeated, determining only the content of Mg(II), so that the amount of Ca(II) was quantified as the difference between the total and the amount of Mg(II). The increase in the final bioadsorbent, obtained after the chemical treatment of orange peel, was in the order of 100% compared to the initial content.

## 2.3 Determination of the efficiency of the prepared bioadsorbent

The verification of the characteristics of the bioadsorbent obtained was done with a series of synthetic Cu(II) solutions. Initially, the adsorption of Cu(II) by the mass of the bioadsorbent prepared in solutions was qualitatively tested by classical analytical chemistry tests.

First, in two test tubes, 25 mL of a CuSO<sub>4</sub> solution with a concentration of 500 mg/L of Cu(II), prepared from CuSO<sub>4</sub>·5H<sub>2</sub>O supplied by Panreac (Barcelona), was introduced in two test tubes. In one of the tubes was introduced 1 gram of the bioadsorbent, previously hydrated for 24 hours. Both tubes were tightly closed and agitated for 10 minutes in a mobile-rod model roller agitator, supplied by the company Selecta (Barcelona). After this time, the bioadsorbent acquired a green color. A 5 mL aliquot was extracted from the liquid contained in both test tubes and 5 mL reacted from a 5% (w/v) KI solution.

A change in color was observed in the aliquot from the test tube that did not contain bioadsorbent due to iodine formation. 5 mL of dichloromethane were added to each tube, stirred vigorously and then left at rest. A pink coloration of the organic phase confirmed the formation of iodine (Figure 2).



**FIGURE 2: Left) Aliquot without bioadsorbent. Right) Aliquot with bioadsorbent.**

Established the viability of this bioadsorbent as a cation exchanger, the lower limit of bioadsorbent was established capable of keeping the organic phase colourless. To do this, a series of 8 test tubes was prepared. In each of them, 25 mL of the 500 mg/L dissolution of Cu(II) and a variable amount of bioadsorbent, previously hydrated for 24 hours, was introduced. The amounts of bioadsorbents added were: 0,25; 0,50; 0,75; 1,00; 1,25; 1,50; 1,75 and 2,00 g and repeated the extraction process described above. From the concentration of 1.25 g of bioadsorbent / 25 mL of solution of 500 mg / L of Cu (II), no color was observed in the dichloromethane phase.

Another series of 8 test tubes was then prepared. As a precautionary measure, 1,5 g of bioadsorbent/25 mL of Cu(II) dissolution solution work was established as a working concentration. Selected Cu(II) concentrations were: 2000; 1000; 750; 500; 250; 125; 50; and 25 mg/L. Coloration was only seen in the dichloromethane phase for concentrations greater than 500 mg/L of Cu(II).

## 2.4 Batch Experiences

Two series of samples were prepared with a variable Cu(II) concentration. The first group included Cu(II) solutions of concentrations greater than 250 mg/L. The second consisted of solutions from Cu(II) up to 250 mg/L.

As a precautionary measure, 1,5 g of bioadsorbent/100 mL of Cu(II) dissolution solution work was established as a working concentration. This amount of bioadsorbent, previously hydrated for 24 hours, was in contact with the corresponding dissolution of Cu(II), inside a tightly sealed container with agitation for 15 minutes.

In the first group of solutions, the percentage of unadsorbed Cu(II) was determined by a redox volumetry, using as a thiosulphate 0.1M solution prepared from  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  supplied by the company Panreac (Barcelona). In the second group of solutions, the concentration of unadsorbed Cu(II) was determined by an AA-6300 SHIMADZU atomic absorption spectrophotometer.

Table 2 shows the results obtained with samples from the first group, with Cu(II) concentrations greater than 500 mg/L. The volumes of titration agent used in the absence and presence of bioadsorbent are detailed.

**TABLE 2**  
**PERCENTAGE OF BIOADSORPTION IN SAMPLES OF [Cu(II)] > 250 mg/L**

[Cu(II)] (mg/L) -α-	mg Cu(II) absolutes	mL $\text{Na}_2\text{S}_2\text{O}_3$ without bioadsorbent	mL $\text{Na}_2\text{S}_2\text{O}_3$ with bioadsorbent	mg/L Cu(II) bioadsorbed	% Cu(II) bioadsorbed	mg Cu(II)/g bioadsorbent -β-	$\gamma=\alpha/\beta$
4000	400	15.3	9.8	1437.9	35.95	95,86	41,72
3000	300	11.5	6.9	1200.0	40.00	80,00	37,50
2500	250	10	5.3	1175.0	47.00	78,30	31,93
2000	200	7.2	3.5	1027.8	51.39	68,52	29,19
1500	150	5	2.3	810.0	54.00	54,00	27,78
1000	100	3.8	1.3	657.9	65.79	43,86	22,80
750	75	2.8	0.7	562.5	75.00	37.50	20,00
500	50	2	0.1	475.0	95.00	31.70	15,77

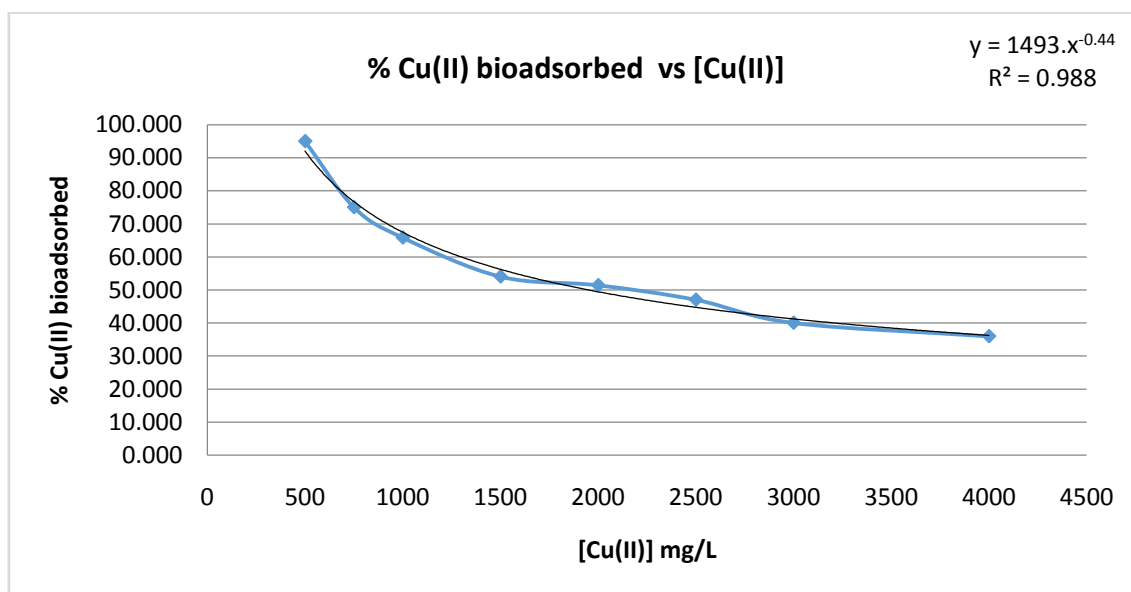
Table 3 shows the results obtained by atomic absorption spectrometry.

**TABLE 3**  
**PERCENTAGE OF BIOADSORPTION IN SAMPLES OF [Cu(II)] < 250 mg/L**

[Cu(II)] <sub>o</sub> (mg/L) -α-	mg Cu(II) absolutes	[Cu(II)] <sub>f</sub> mg/L (AA)	mg/L Cu(II) bioadsorbeds	% Cu(II) bioadsorbed	mg Cu(II)/g bioadsorbent -β-	$\gamma=\alpha/\beta$
5	0.5	1.73	3,27	65,4	0.22	22.73
10	1	0.98	9,02	90,2	0.60	16.67
25	2.5	2.26	22,74	91,0	1.52	16.45
50	5	2.79	47,21	94,4	3.15	15.87
100	10	4.36	95,64	95,6	6.38	15.67
250	25	8.14	241,86	96,7	16.12	15.51

Selected Cu(II) concentrations were: 5; 10; 25; 50; 100 and 250 mg/L. The concentration of unadsorbed Cu(II) was determined by an AA-6300 SHIMADZU atomic absorption spectrophotometer. The ratio of Cu(II) to the initial concentration of Cu(II) to bioadsorbed Cu(II) mg/L per gram of bioadsorbent confirms that this cation exchange takes place through a balancing process.

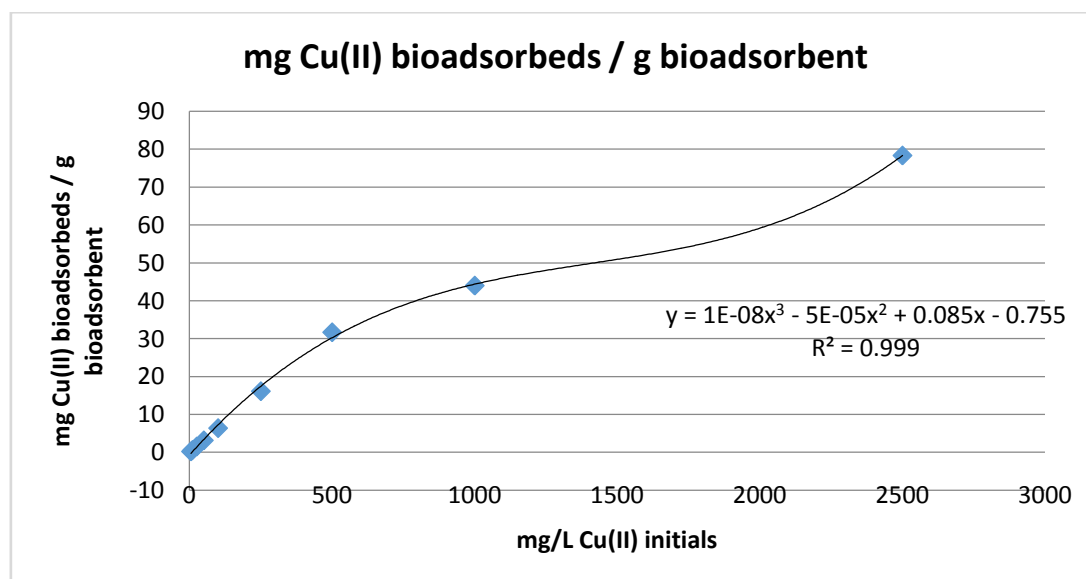
The corresponding graphical representation of the bioadsorbed Cu(II) % from the initial concentration of Cu(II) (Figure 3) shows a bioadsorbent saturation process.



**FIGURE 3: % Cu(II) bioadsorbed in solutions greater than 250 mg/L of Cu(II)**

The joint representation of the mg of Cu (II) bioadsorbed / gram of bioadsorbent from both experimental series is shown in Figure 4.

A polynomial trend line of order 3 is observed. This isotherm can be adjusted to the BET equation (Brunauer et al, 1938). As a result, it can be admitted that the adsorbate covers the adsorbent until a monolayer is formed and the process continues with multilayer adsorption. However, only the values for concentrations less than 250 mg/L of Cu(II) are considered to conform to the equation of (Langmuir, 1916). This model considers that, for the adsorption of metal ions, retention initially increases in a linear way. This retention is limited by the number of active sites available and therefore a maximum of adsorption related to the formation of the adsorbate monolayer on the adsorbent surface is reached.



**FIGURE 4: mg Cu(II) bioadsorbeds/gram bioadsorbent vs mg/L Cu(II) initials**

## 2.5 pH influence

Established that the adsorption process takes place through a balance between the adsorbent and the adsorbate, the pH influence was determined. The pH of the aqueous solution is an important parameter that controls the adsorption processes of metals in different adsorbents due to the fact that hydrogen ions are constituted are a strongly competitive adsorbate.

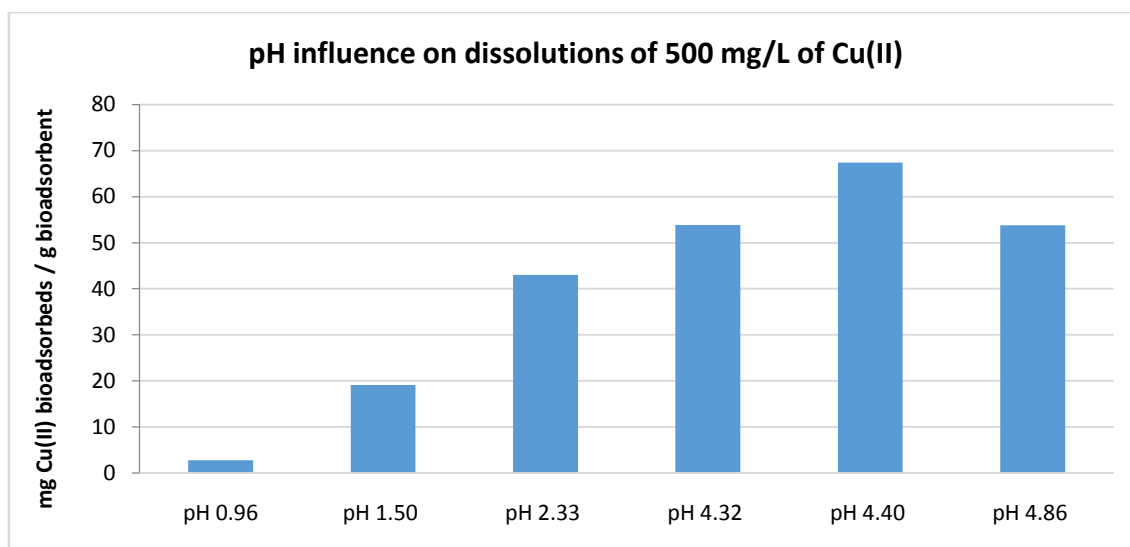
A series of samples with a constant Cu(II) concentration of 500 mg/L was prepared. The pH values were: 0,96; 1,50; 2,33; 4,32; 4,40 and 4,86. Each of these solutions was kept in agitation for 15 minutes inside a hermetically sealed container containing 1,5 g of bioadsorbent.

The influence of pH on the adsorption process can be seen in Figure 5. At values below 2,33 pH units, the colour of the bioadsorbent shows that hydrogen ions prevent adsorption of the Cu(II). Above this value, the green coloration acquired by the bioadsorbent showed that the Cu(II) had been predominantly adsorbed.



**FIGURE 5. Cu(II) solutions of 500 mg/L in contact with the bioadsorbent at different pH values (0,96; 1,50; 2,33; 4,32; 4,40; 4,86).**

Figure 6 shows the mg values of Cu(II) bioadsorbeds/gram of bioadsorbent to the different pH values. The maximum bioadsorption value of Cu(II) was observed at a pH 4.4. This value was achieved with a regulatory solution of 0,1M acetic acid/sodium acetate.



**FIGURE 6. mg of Cu(II) bioadsorbeds/gram of bioadsorbent at different pH values.**

The values in Table 4, analogous to Table 3, show the influence of performing the pH-regulated experience. A smaller dispersion in the coefficient values can be seen.

**TABLE 4**  
**PERCENTAGE OF BIOADSORPTION IN SAMPLES OF [Cu(II)]- 100 mg/L at pH 4.4**

[Cu(II)] <sub>0</sub> (mg/L) -α-	mg Cu(II) absolutes	[Cu(II)] <sub>f</sub> mg/L (AA)	mg/L Cu(II) bioadsorbeds	% Cu(II) bioadsorbed	mg Cu(II)/ g bioadsorbent -β-	γ=α/β
5	0.5	1.24	3,76	75,2	0.25	20,00
10	1	2.32	7,68	76,8	0.51	19,61
25	2.5	5.69	19,31	77,2	1,29	19,38
50	5	9.95	40,05	80,1	2,67	18,73
100	10	18.95	81,05	81,05	5,4	18,51

The high observed affinity between bioadsorbent and Cu(II) under controlled pH conditions resulted in the desorption process only being effective when treating the depleted bioadsorbent with HCl, obtaining a dissolution of  $\text{CuCl}_2$ .

Alternatively, the bioadsorbent was calcined with depleted at 570 °C inside a Hobersal JB 20 laboratory muffle furnace for 4 hours. The analysis of the resulting ash made it possible to verify that the Cu(II) was in the form of copper oxide ( $\text{CuO}$ ).

## 2.6 Continuous experiences

Typically, the texture or degree of consistency of the bioadsorbent is a considerable limitation to take into account the proper functioning of an adsorption column.

Before passing the Cu(II) solution through the adsorption column, the adsorbent was hydrated with distilled water in order to avoid a sudden decrease in the concentration of Cu(II) in the outlet solution, due to a rapid adsorption of the metal by dry biomass, especially at the first time it makes contact with the solution (Vieira et al., 2008). They were hydrated in the order of 250 grams of bioadsorbent, to have enough for the different experiences in continuous.

In the continuous experiences, two standard adsorption columns were used, a small one, AFORA 5831, with porous plate No. 0 and a glass wrench with a 2/3 mm pin, an internal diameter of 10 mm and a useful length of 200 mm; and a larger column for prepare chromatography, AFORA 5855, with 2 29/32 frosted adapters, 30 mm internal diameter, built-in No. 0 porous plate and a glass wrench with a 2/3 mm pass and a useful length of 500 mm.

In a first experience, column AFORA 5831 was used. Inside, 5 grams of bioadsorbent were introduced that had previously been hydrated with distilled water for 24 hours.

To establish optimal elution conditions, three Cu(II) solutions of 500 and 100 mg/L were prepared and introduced by the upper end with the help of a peristaltic pump a WATSON MARLOW 505S. Three flow rates were used: 6,5; 13; 26 rpm corresponding to 6,36; 12,95 and 26.04 mL/min.

The first dissolution to be eluted was 500 mg/L of Cu(II). In all three flows a homogeneous elution front was observed, reaching the saturation of the column. When the dissolution of 100 mg/L was used, the saturation of the spine was also reached. However, the elution at 6,5 rpm did not show a homogeneous elution front. This phenomenon was associated with the formation of air bubbles both inside the column and in the container where the bioadsorbent had been hydrated. From the different stages of the chemical treatment to which the orange peel is subjected until it becomes the final bioadsorbent, the alkaline treatment causes a solvation and saponification process. As a result, biomass expands, originates channels, and becomes more accessible to enzymes and bacteria (Fengel & Wegener, 1984).

Table 5 lists the volumes that were eluted, in all of the experiences, until the saturation of the column, that is, that the concentration of Cu(II) of the eluent that came out from the lower end of the column coincided with the concentration of Cu(II) that was introduced by the upper end by the peristaltic pump.

**TABLE 5**  
**SATURATION VOLUME OF 5 g BIOADSORBENT**

Revolutions used	Saturation volume [Cu(II)] <sub>o</sub> = 500 mg/L	Saturation volume [Cu(II)] <sub>o</sub> = 100 mg/L
6,5 rpm	700 mL	2400 mL
13 rpm	600 mL	2200 mL
26rpm	500 mL	2100 mL

Spanish Royal Decree 140/2003 (Ministry Presidency, 2003) states that the permitted limit of Cu(II) in water for human consumption is 2 mg/L. For this reason, the main objective of ongoing experiences was to determine the volume eluted or cutting volume when the Cu(II) concentration was 2 mg/L.

In this case, the AFORA 5855 column was used and the concentration of Cu(II) dissolution was set at 40 mg/L and the amount of bioadsorbent used was 15 grams, previously hydrated.

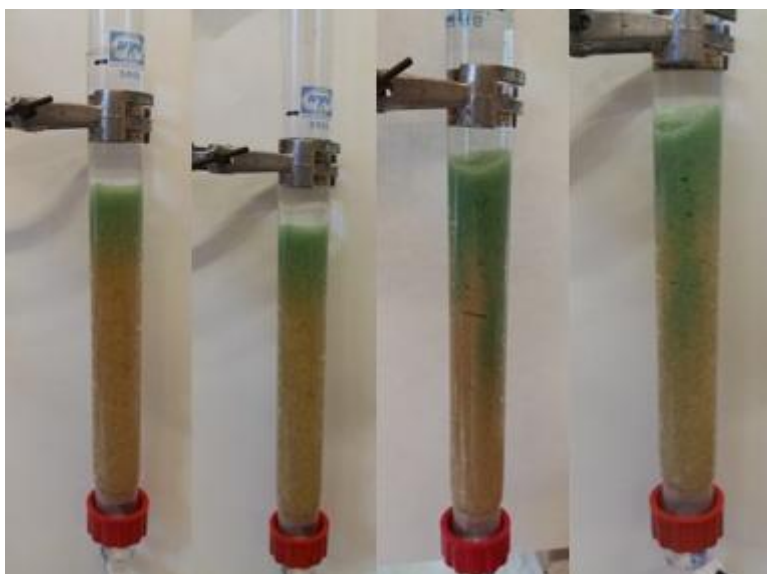
During the realization of this experience, the formation of channels was again evident (see Figure 7). As a result, the bioadsorbent was thermally modified.



First, a part of the bioadsorbent that had initially dried at 32°C was kept at 75°C for 24 hours, with the purpose of eliminating or decreasing the formation of bubbles. In this way it was hoped to achieve an elution with a homogeneous front.

After this heat treatment, the bioadsorbent was hydrated for three days with distilled water in an airtight container. Although the formation of bubbles was observed, a phenomenon attributed to the existence of a fermentation process, a homogeneous elution front was achieved when the dissolution of 40 mg/L of Cu(II) was eluted.

In view of these results, it was chosen to increase the temperature. Thus, another fraction of the bioadsorbent that had been dried at 32 °C was kept at 110 °C for 24 hours. In this case, the hydration process was performed in duplicate, with distilled water and with a regulatory solution of 0,1M acetic acid-sodium acetate of pH 4.4.



**FIGURE 7. Elution of a 40 mg/L Cu(II) solution with a flow rate of 26,04 ml/min**

The elution was performed with a 40 mg dissolution of Cu(II) in distilled water and with a dissolution of 40 mg/L of Cu(II) to pH 4,4. In both cases a homogeneous elution front was achieved and the formation of bubbles was not observed, using a flow rate of 26, 04 mL/min.

Table 6 shows the values of the volumes eluted when the concentration of Cu (II) was 2 mg / L, obtained with the bioadsorbent treated at 75 °C and with the two variations of the bioadsorbent treated at 110 °C. The flow rate used was 26.04 mL / min (26 rpm). It highlights the importance of heat treatment and pH regulation.

**TABLE 6**

**ELUTED VOLUME UNTIL REACHING A CONCENTRATION OF 2 mg / L Cu (II) FROM AN INITIAL SOLUTION OF 40 mg / L Cu(II)**

	Eluted volume (*)	Eluted volume /g bioadsorbent
Dried bioadsorbent at 75 °C	5300 mL	353 mL
Dried bioadsorbent at 110 °C	7900 mL	527 mL
Dried bioadsorbent at 110°C with pH	9800 mL	653 mL

(\*) flow used: 26,04 mL/min

### III. DISCUSSION

Bioadsorption is a process that began to be implemented in the early 1990s in order to remove pollutants from wastewater from the industrial sector; over the years, research has mainly focused on the use of living and/or dead biomass. However, the results shown as the best alternative the materials derived from dead biomass, for its economic and maintenance advantages, it is emphasized that the use of dead biomass prevents the nutrient supplement and eliminates the problem of toxicity, in addition, the adsorption process is not interrupted by the death of the biomass due to the high concentrations of pollutants inside them (He & Chen 2014).

However, bioadsorption has not been widely used in large-scale commercial applications. Key factors affecting the growth and evolution of bioadsorption as a practical technology for wastewater decontamination include: lack of research on multi-

component and wastewater solutions with complex matrix effects, incomplete understanding of the physicochemical characteristics of biomass of different types and non-integration of bioadsorption into wastewater treatment plants (Vijayaraghan & Balasubramanian, 2015)

The cell walls of bioadsorbent materials contain polysaccharides, proteins and lipids, and therefore numerous functional groups capable of binding heavy metals on their surface. Functional groups present include the amino, carboxylic, hydroxylic, phosphate and thiol groups that differ in their affinity and specificity with respect to susceptibility to bind to the different metal ions (Ghimire et al., 2003). The adsorption takes place mainly inside the particles, on the walls of the pores at specific points. The retention mechanism initially occurs with the migration of the sorbate from the solution to the surface of the sorbent, followed by a diffusion process to end at fixation at the active site (Hosfall & Abia, 2003).

The removal of metals by treated pectin is basically due to a phenomenon of ion exchange between Ca(II) and metal ions in solution until a balance is achieved. In this way the Ca(II) attached to the polygalacturonic chains is displaced by the metal ion until the equilibrium concentrations are reached in both phases. Ionic exchanger groups are carboxylic groups in this metal/calcium ion exchange process (Cardona Gutierrez, 2013). Consequently, bioadsorption depends on the protonation or deprotonation of these carboxylic groups. At low pH values cell wall ligands are associated with hydronium ions ( $H_3O^+$ ) that restrict access to metal ion ligands as a result of repulsive forces.

The most commonly used system for the continuous bioadsorption study has been fixed bed. In this, the particles of the bioadsorbent allow the passage of the fluid without separating from each other, causing the height of the bed and, consequently, its porosity to remain constant. Column saturation is controlled by parameters such as time, space, and column size, (Kratochvil & Volesky, 1988). This system turns out to be the most effective for heavy metal removal. Regeneration of bioadsorbents increases the economics of the process by allowing their reuse in multiple adsorption cycles (Volesky, 2001). However, when the biomass becomes saturated and becomes a hazardous waste it becomes necessary to inactivate it.

Dry calcination is shown as an alternative for handling, because bioadsorption is a process that allows metals to be encapsulated in the biological matrix and prevents them from being released generating a new pollution problem, while reducing the volume and mass of residual material (Carrillo et al. 2012) (Vizcaíno & Fuentes Molina, 2015).

#### IV. CONCLUSION

Checked:

- The importance of particle size in the chemical treatment of orange peel (500-1000  $\mu m$ ).
- The importance of a correct elimination of organic matter in acid attack (elimination of non-methylated pectin and carbohydrates) to prevent the formation of a bioadsorbent in the form of a gel that makes it difficult to exchange cationic both in batch and continuous.
- The development of microorganisms in the final bioadsorbent mass subjected to a period of three or more days of hydration.

It has been determined:

- Adjustment to the Langmuir model at concentrations below 250 mg/L of Cu(II).
- Adjustment to the Brunauer model when concentrations below 250 mg/L of Cu(II) have been taken into account together in conjunction with those above 250 mg/L of Cu(II).
- The temperature necessary to prevent the development of microorganisms has been to heat treat the final bioadsorbent for a period of 24 hours at 110°C.
- Optimal pH for Cu(II) bioadsorption at 4,4 pH units.

It has been established:

- The final bioadsorbent, dried at 110 °C, at pH 4,4 has a yield of 653 mL/g bioadsorbent to reduce an initial concentration of 40 mg/L of Cu(II) to a final concentration of 2 mg/L in a continuous process with a flow rate of 26,04 mL/min.

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